

WHAT IS CLAIMED IS:

1. A process for the production of a liquid hydrocarbon oil, comprising the steps of:

- 5 (a) mixing a gas feed, containing a lower hydrocarbon having 1-4 carbon atoms and 10-50 mole % of CO₂ based on a total mole of the CO₂ and the lower hydrocarbon, with H₂O to obtain a mixed gas having contents of the CO₂, H₂O and lower hydrocarbon satisfying
10 the following condition:

$$0.5 \leq ([CO_2] + [H_2O])/[C] \leq 2.5$$

wherein [CO₂] represents the moles of the CO₂, [H₂O] represents the moles of the H₂O and [C] represents the moles of carbon of the lower hydrocarbon;

- 15 (b) contacting said mixed gas with a catalyst at a temperature of 600-1,000°C and a pressure of 10-75 atm to produce a synthesis gas with a carbon conversion efficiency Cf of at least 50 % and a synthesis gas production efficiency Yf of at least 80 %,

- 20 said synthesis gas production efficiency Yf being represented by the following formula:

$$Yf = \{([CO] + [H_2])/([C] + [CO_2] + [H_2O])\} \times 100 \%$$

- wherein [CO] represents the moles of CO in said synthesis gas, [H₂] represents the moles of H₂ in said synthesis gas,
25 and [CO₂], [H₂O] and [C] are as defined previously,

said carbon conversion efficiency Cf being represented by the following formula:

$$Cf = \{[CO]/([C] + [CO_2])\} \times 100 \%$$

wherein [CO], [CO₂] and [C] are as defined previously,

- 30 said synthesis gas having a molar ratio of hydrogen to carbon monoxide of 1.5-2.5,

- said catalyst having a specific surface area of 5 m²/g or less and comprising a magnesium oxide-containing carrier and at least one catalytic metal selected from the
35 group consisting of rhodium and ruthenium and supported on

said carrier in an amount of 10-5,000 ppm, in terms of elemental metal, based on the weight of said carrier;

(c) reacting said synthesis gas in the presence of a Fischer-Tropsch catalyst having a low CO shift reaction activity to obtain a product containing a liquid hydrocarbon oil; and

(d) separating said liquid hydrocarbon oil from said product.

10 2. A process as claimed in claim 1, wherein said gas feed contains 20-40 mole % of CO₂ and wherein said mixed gas satisfies the following condition:

$$1 \leq ([\text{CO}_2] + [\text{H}_2\text{O}]) / [\text{C}] \leq 2$$

wherein [CO₂], [H₂O] and [C] are as defined in claim 1.

15

3. A process as claimed in claim 1, wherein said gas feed is discharged overhead from a distillation tower where a raw material feed containing CO₂ and a lower hydrocarbon is distilled at a pressure of 10-80 atm while removing CO₂ from a bottom thereof.

20

4. A process as claimed in claim 3, wherein said distillation tower is operated at a pressure of 20-50 atm and a tower top temperature of -60°C.

25

5. A process as claimed in claim 1, wherein said Fischer-Tropsch catalyst comprises Co and/or Ru as catalytic metal thereof.

30 6. A process as claimed in claim 1, further comprising subjecting said liquid hydrocarbon oil separated in step (d) to catalytic hydrogenation and/or catalytic hydrocracking to obtain gasoline, kerosene and gas oil.

35 7. A process as claimed in claim 1, further comprising

separating a gas product containing methane, hydrogen and carbon dioxide from said product in step (d), and using at least part of said gas product as a heat energy source in step (b).

5

8. A process as claimed in claim 1, further comprising separating a light hydrocarbon fraction containing olefins from said product in step (d), and recycling at least part of said light hydrocarbon fraction to step (c).

10

9. A process for the production of dimethyl ether, comprising the steps of:

(a) mixing a gas feed, containing a lower hydrocarbon having 1-4 carbon atoms and 30-70 mole % of CO₂ based on a total mole of the CO₂ and the lower hydrocarbon, with H₂O to obtain a mixed gas having contents of the CO₂, H₂O and lower hydrocarbon satisfying the following condition:

$$0.5 \leq ([CO_2] + [H_2O])/[C] \leq 2.5$$
wherein [CO₂] represents the moles of the CO₂, [H₂O] represents the moles of the H₂O and [C] represents the moles of carbon of the lower hydrocarbon;

(b) contacting said mixed gas with a catalyst at a temperature of 600-1,000°C and a pressure of 10-75 atm to produce a synthesis gas with a synthesis gas production efficiency Y_f of at least 80 % and a carbon conversion efficiency C_f of at least 50 %,

said synthesis gas production efficiency Y_f being represented by the following formula:

$$Y_f = \{[CO] + [H_2]\} / ([C] + [CO_2] + [H_2O]) \times 100 \%$$
wherein [CO] represents the moles of CO in said synthesis gas, [H₂] represents the moles of H₂ in said synthesis gas, and [CO₂], [H₂O] and [C] are as defined previously,

said carbon conversion efficiency C_f being represented by the following formula:

$$Cf = \{[CO]/([C] + [CO_2])\} \times 100 \%$$

wherein [CO], [CO₂] and [C] are as defined previously,

said synthesis gas having a molar ratio of hydrogen to carbon monoxide of 0.5-1.5,

5 said catalyst having a specific surface area of 5 m²/g or less and comprising a magnesium oxide-containing carrier and at least one catalytic metal selected from the group consisting of rhodium and ruthenium and supported on said carrier in an amount of 10-5,000 ppm, in terms of
10 elemental metal, based on the weight of said carrier;

(c) reacting said synthesis gas in the presence of one or more catalysts having activities of methanol synthesis, methanol dehydration and CO shift reaction to obtain a product containing dimethyl ether; and

15 (d) separating said dimethyl ether from said product.

10. A process as claimed in claim 9, wherein said gas feed contains 40-60 mole % of CO₂ and wherein said mixed gas satisfies the following condition:

20 $1 \leq ([CO_2] + [H_2O])/[C] \leq 2$

wherein [CO₂], [H₂O] and [C] are as defined in claim 9.

11. A process as claimed in claim 9, wherein said gas feed is discharged overhead from a distillation tower
25 where a raw material feed containing CO₂ and a lower hydrocarbon is distilled at a pressure of 10-80 atm while removing CO₂ from a bottom thereof.

12. A process as claimed in claim 11, wherein said
30 distillation tower is operated at a pressure of 20-50 atm and a tower top temperature of -60°C.

13. A process as claimed in claim 9, wherein step (c) is performed using at least two catalysts selected from the
35 group consisting of a methanol synthesis catalyst, a

methanol dehydration catalyst and a CO shift reaction catalyst.